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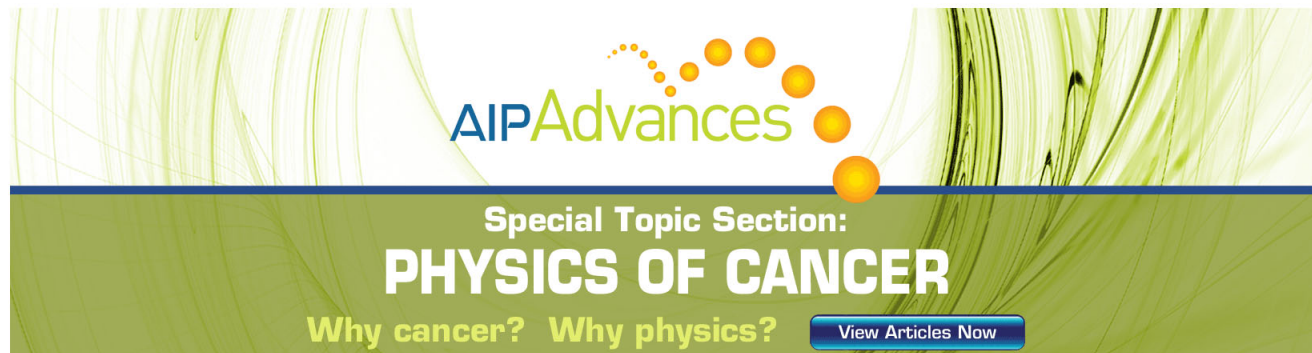
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# A theory for time-dependent solvation structure near solid-liquid interface

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We propose a theory to describe time-dependent solvation structure near solid-liquid interface. Recently, we have developed two-dimensional-reference interaction site model to describe solvation structure near solid-liquid interface at the equilibrium state. In the present study, the theory is extended to treat dynamical aspect of the solvation; site-site Smoluchowski-Vlasov equation and surrogate Hamiltonian description are utilized to deal with the time-dependency. This combination enables us to access a long-time behavior of solvation dynamics. We apply the theory to a model system consisting of an atomistic wall and water solvent, and discuss the hydration structure dynamics near the interface at the molecular-level. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4729750>]

## I. INTRODUCTION

Solvation dynamics near solid-liquid interface has been extensively studied for a long time. Studies using cyclic voltammetry and impedance spectroscopy have shown that dynamical behavior of solution is crucial to understand chemical process near the interface.<sup>1–3</sup> According to a recent development of experimental methods, the dynamics has been revealed at the molecular-level.<sup>4–16</sup> For example, McGuire and Shen investigated vibrational dynamics of water near the interface of silica with time-resolved sum-frequency vibrational spectroscopy.<sup>11</sup> Yamakata and Osawa investigated the dynamics of water molecules on CO-covered Pt electrode using laser-induced temperature jump method.<sup>13</sup>

Theoretical and computational methods also provide valuable insights by usually considering a solid as an atomistic wall. Molecular dynamics (MD) simulation is a representative of the methods, and the molecular-level knowledge that cannot be obtained with the experimental methods, has been accumulated.<sup>17–21</sup> Time-dependent density functional theory has been also successfully applied to investigate the solvation dynamics.<sup>22,23</sup> Senapati *et al.* studied the polarization relaxation of liquid consisting of dipolar hard sphere near the interface by the theory.<sup>24–26</sup> Reference interaction site model (RISM) theory is a statistical mechanics for molecular liquids, and can be regarded as an alternative to MD simulation.<sup>27–31</sup> One of the differences from MD simulation is that the RISM theory analytically treats an ensemble of infinite number of solvent molecules. In other words, the RISM theory is free from the so-called sampling problem. The theory has been successfully applied to solvation of various systems such as hydration of protein.<sup>29,32–40</sup> Recently, we proposed a two-dimensional (2D)-RISM theory for solvation structure near solid-liquid interface at the equilibrium state.<sup>41</sup>

Although original RISM is a theory for static property, related theories to describe solvation dynamics are also available. Site-site Smoluchowski-Vlasov (SSSV) equation,

which is essentially a diffusion equation for molecular liquid, is solved utilizing the solution of the RISM theory.<sup>42,43</sup> The equation has been successfully applied to describe the van Hove time correlation function of pure solvents such as water and acetonitrile. The linear response theory is applicable to the non-equilibrium state using time correlation function of the equilibrium state.<sup>30,44</sup> Raineri and co-workers proposed surrogate Hamiltonian description, which is regarded as an extended linear response theory.<sup>45–47</sup> The theory is also solved using the solution of RISM theory and is guaranteed that the state appropriately converges to the final equilibrium state at  $t$  (time)  $\rightarrow \infty$ . The theory is thus accessible to long-time solvation dynamics, which is one of the remarkable advantages compared to MD simulation. The surrogate Hamiltonian description requires the van Hove function as input. Ishida *et al.* utilized the SSSV equation to obtain the van Hove function and applied the surrogate description to solvation dynamics around benzonitrile and pyridinium *N*-phenoxide after the vertical excitation.<sup>48,49</sup> In this study, we propose a theory to treat solvation dynamics near solid-liquid interface. This theory utilizes the surrogate Hamiltonian description and the SSSV equation. The remarkable feature of the theory is to treat the solvation dynamics as time-dependent 2D density distribution, which focuses on the anisotropic solvation structure near the interface.

In Sec. II, we first briefly explain the 2D-RISM theory that describes the 2D density distribution in the equilibrium state, because its solution is required to treat solvation dynamics. Note that the original 2D-RISM theory is applicable only for static properties, and the time-dependency cannot be treated. We then propose a new formula to describe the time-dependent 2D density distribution based on the surrogate Hamiltonian description. To obtain the van Hove function required as an input in the proposed formula, the SSSV equation is employed. Thanks to their analytical feature, distribution function at arbitrary time  $t$  is available with the same computational cost. We apply the proposed theory to the system in which an atomistic wall is immersed in water solvent. Solvation dynamics near the wall-water interface is discussed at the atomic-level.

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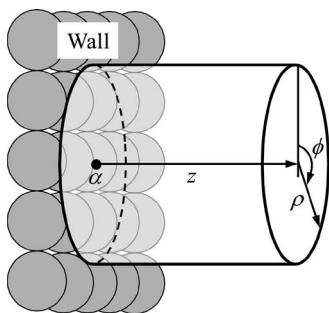


FIG. 1. Cylindrical coordinate system.

## II. THEORY

### A. 2D-RISM theory

The 2D-RISM theory describes the 2D density distribution near the interface in an equilibrium state. Since a detailed explanation of the theory is given in the previous paper,<sup>41</sup> only the essential points are summarized. The 2D distribution function is expressed with the cylindrical coordinate system shown in Fig. 1. An origin of the coordinate system is defined as a position of an arbitrary site  $\alpha$  in the wall. An axis perpendicular to the wall is  $z$  axis,  $\rho$  is distance from the  $z$  axis on a plane parallel to the wall, and  $\phi$  is an angle along the wall. In this coordinate system, the position of a solvent site  $\eta$  ( $\mathbf{r}_\eta$ ) is treated with a vector  $\mathbf{r}_{\alpha\eta} (= \mathbf{r}_\eta - \mathbf{r}_\alpha) = \{\rho_{\alpha\eta}, z_{\alpha\eta}, \phi_{\alpha\eta}\}$ , where  $\mathbf{r}_\alpha$  is the position of wall site  $\alpha$ .

Using the analogous procedure to derive RISM equation,<sup>29-31</sup> 2D-RISM equation in the reciprocal ( $\mathbf{k}$ ) space is given as follows:<sup>41</sup>

$$h_{\alpha\eta}(k^\rho, k^z) = \sum_{\alpha'\eta'} w_{\alpha\alpha'}(k^\rho, k^z) \tilde{c}_{\alpha'\eta'}(k^\rho, k^z) \times [\omega_{\eta'\eta}^V(|\mathbf{k}|) + n^V h_{\eta'\eta}^V(|\mathbf{k}|)], \quad (1)$$

where  $k^\rho$  and  $k^z$  are the  $\rho$ - and  $z$ -components of  $\mathbf{k}$ .  $h_{\alpha\eta}$  is the 2D total correlation function between sites  $\alpha$  and  $\eta$ ,  $c_{\alpha\eta}$  is the 2D direct correlation function between sites  $\alpha$  and  $\eta$ ,  $\omega_{\eta'\eta}^V$  is the intramolecular correlation function of solvent, and  $h_{\eta'\eta}^V$  is the site-site total correlation function of bulk solvent.  $\omega_{\eta'\eta}^V$  and  $h_{\eta'\eta}^V$  have the same meanings as those used in the original RISM equation.<sup>27-31</sup>  $w_{\alpha\alpha'}$  in Eq. (1) is the 2D-intramolecular correlation function of the wall written as

$$w_{\alpha\alpha'}(k^\rho, k^z) = e^{ik^z \cdot z_{\alpha\alpha'}} J_0(k^\rho \rho_{\alpha\alpha'}), \quad (2)$$

where  $J_0$  is the 0th Bessel function.

As seen from Eq. (1), the equation to be solved is a matrix equation whose matrix size is dependent on the number of wall sites. But the size is drastically reduced by combining with polymer-RISM equation.<sup>32-36</sup> Each unit of the wall is here labeled as  $\alpha_i$  ( $i = 1, \dots, N$ ) consisting of a finite set of atomic sites  $\{\alpha_i, \alpha'_i, \dots, \alpha_i^{(M)}\}$ . If respective units are equivalent to each other, Eq. (1) is rewritten as

$$h_{\alpha\eta}(k^\rho, k^z) = \sum_{\alpha'\eta'} W_{\alpha\alpha'}(k^\rho, k^z) \tilde{c}_{\alpha'\eta'}(k^\rho, k^z) \times [\omega_{\eta'\eta}^V(|\mathbf{k}|) + n^V h_{\eta'\eta}^V(|\mathbf{k}|)], \quad (3)$$

where the subscript  $i$  is omitted from  $\tilde{c}_{\alpha_i\eta}$  and  $h_{\alpha_i\eta}$  because of the identity, and the summation over the units is required only once to obtain the new intramolecular correlation function  $W_{\alpha\alpha'}$  given as

$$W_{\alpha\alpha'}(k^\rho, k^z) = \frac{1}{N} \sum_{ij} w_{\alpha_i\alpha'_j}(k^\rho, k^z). \quad (4)$$

To relate the two unknown functions in Eq. (3),  $\tilde{c}_{\alpha\eta}$  and  $h_{\alpha\eta}$ , the following KH-type closure<sup>29,38</sup> is adopted:

$$g_{\alpha\eta}(\rho_{\alpha\eta}, z_{\alpha\eta}) = \begin{cases} \exp\{\chi_{\alpha\eta}(\rho_{\alpha\eta}, z_{\alpha\eta})\} & \text{for } \chi_{\alpha\eta}(\rho_{\alpha\eta}, z_{\alpha\eta}) \leq 0 \\ \chi_{\alpha\eta} + 1 & \text{for } \chi_{\alpha\eta}(\rho_{\alpha\eta}, z_{\alpha\eta}) > 0 \end{cases} \quad (5)$$

$$\chi_{\alpha\eta}(\rho_{\alpha\eta}, z_{\alpha\eta}) = -\beta u_{\alpha\eta}(\rho_{\alpha\eta}, z_{\alpha\eta}) + h_{\alpha\eta}(r_{\alpha\eta}, z_{\alpha\eta}) - \tilde{c}_{\alpha\eta}(\rho_{\alpha\eta}, z_{\alpha\eta}),$$

where  $g_{\alpha\eta}(\rho_{\alpha\eta}, z_{\alpha\eta}) = h_{\alpha\eta}(\rho_{\alpha\eta}, z_{\alpha\eta}) + 1$  is a 2D pair correlation function (2D-PCF) between the wall site  $\alpha$  and the solvent site  $\eta$ ,  $\beta = 1/k_B T$ ,  $k_B$  is Boltzmann's constant, and  $u_{\alpha\eta}$  is the interaction potential between  $\alpha$  and  $\eta$  given as the sum of coulombic and Lennard-Jones terms.

### B. Extension to time-dependent solvation structure

Solvation dynamics treated in this study is as follows. At time  $t < 0$ , the solvent is in equilibrium with the wall in a precursor state (P). At  $t = 0$ , the wall state is suddenly changed from P to a successor state (S), for example, by charging the wall. The solvent responds to the  $P \rightarrow S$  transition, and relaxes to the new equilibrium state. The dynamical response

of solvent is here described by the time-dependent 2D-PCF ( $g_{\alpha\eta}(\rho_{\alpha\eta}, z_{\alpha\eta}, t)$ ) with the surrogate Hamiltonian description.

Since the framework of surrogate Hamiltonian description for 1D distribution function has been already described in detail by Raineri and co-workers,<sup>45-47</sup> we here omit the details of derivation. In the surrogate Hamiltonian description, the distribution function of solvent in an equilibrium state is assumed to be described by a linear equation with respect to a wall-solvent coupling  $\delta\hat{\Psi}^D$ ,

$$f^D(\mathbf{\Gamma}) = f^V(\mathbf{\Gamma})[1 - \beta\delta\hat{\Psi}^D], \quad (6)$$

where superscript  $D$  is P or S,  $\mathbf{\Gamma}$  is a set of coordinates and momenta of solvent sites, and  $f^D(\mathbf{\Gamma})$  is the distribution function in the presence of the wall at the state  $D$ .  $f^V(\mathbf{\Gamma})$  is the distribution function of bulk solvent (i.e., in the absence of

the wall), and  $\delta\hat{\Psi}^D$  is written as

$$\delta\hat{\Psi}^D = \hat{\Psi}^D - \int d\mathbf{\Gamma} f^V(\mathbf{\Gamma}) \hat{\Psi}^D, \quad (7)$$

$$\hat{\Psi}^D = \frac{1}{(2\pi)^3} \int d\mathbf{k} \sum_{\alpha\eta} n^V \hat{h}_{\alpha\eta}(\mathbf{k}) \psi_{\alpha\eta}^D(-\mathbf{k}). \quad (8)$$

In Eq. (7), the second term of the right-hand side is vanished because  $f^V(\mathbf{\Gamma})$  does not depend on  $\hat{\Psi}^D$ .  $\hat{h}_{\alpha\eta}(\mathbf{k})$  in Eq. (8) is given as

$$\hat{h}_{\alpha\eta}(\mathbf{k}) = \frac{1}{n^V} \left[ \left\{ \sum_i e^{i\mathbf{k}\cdot\mathbf{r}_{\alpha\eta i}} \right\} - (2\pi)^3 n^V \delta(\mathbf{k}) \right], \quad (9)$$

where  $\mathbf{r}_{\alpha\eta i} = \mathbf{r}_{\eta i} - \mathbf{r}_{\alpha}$ , and  $\mathbf{r}_{\eta i}$  is the position of site  $\eta$  of  $i$ th solvent molecule.

Based on Eq. (6), the non-equilibrium ensemble average of a dynamical variable  $\hat{\mathcal{G}}(t)$  in the condition of  $P \rightarrow S$  transition at  $t = 0$  is given as<sup>45–47</sup>

$$\langle \hat{\mathcal{G}}(t) \rangle_{\Gamma} = \int d\mathbf{\Gamma} f(\mathbf{\Gamma}, t) \hat{\mathcal{G}}(t) = \langle \hat{\mathcal{G}} \rangle_{\Gamma}^S + \beta C(t), \quad (10)$$

where  $f(\mathbf{\Gamma}, t)$  is the time-dependent distribution function of solvent, and

$$\langle \hat{\mathcal{G}} \rangle_{\Gamma}^D = \int d\mathbf{\Gamma} f^D(\mathbf{\Gamma}) \hat{\mathcal{G}} \quad (11)$$

is the ensemble average of static variable  $\hat{\mathcal{G}}$  in the equilibrium state  $D$  ( $= P$  or  $S$ ).  $C(t)$  is the time correlation function defined as

$$C(t) = \int d\mathbf{\Gamma} f^V(\mathbf{\Gamma}) \hat{\mathcal{G}}(t) (\delta\hat{\Psi}^S - \delta\hat{\Psi}^P). \quad (12)$$

Notice that  $\hat{\Psi}^D$  or  $\psi_{\alpha\eta}^D$  (cf. Eq. (8)) is not yet explicitly given. If  $\hat{\Psi}^D$  is given as the *factual* interaction energy between the wall and solvent, such as the sum of coulombic and Lennard-Jones terms, then the standard linear response formula is yielded.<sup>45</sup> In the surrogate Hamiltonian description,  $\psi_{\alpha\eta}^D$  is given as the renormalized potential that gives the static average  $\langle \hat{\mathcal{G}} \rangle_{\Gamma}^D$  (cf. Eq. (11)) identical to the average given without the assumption of Eq. (6).  $\psi_{\alpha\eta}^D$  of the surrogate description for the 2D density distribution function is found from the following equation:

$$\begin{aligned} h_{\alpha\eta}^D(k^{\rho}, k^z) &= \langle \hat{h}_{\alpha\eta}(\mathbf{k}) \rangle_{\Gamma, \phi_{\alpha\eta}}^D \\ &= \left\langle \sum_{\alpha'\eta'} e^{\mathbf{k}\cdot\mathbf{r}_{\alpha\alpha'}} \{ -\beta \psi_{\alpha'\eta'}^D(\mathbf{k}) \} [w_{\eta'\eta}^V(|\mathbf{k}|) + n^V h_{\eta'\eta}^V(|\mathbf{k}|)] \right\rangle_{\phi_{\alpha\eta}}, \end{aligned} \quad (13)$$

where  $\langle \cdots \rangle_{\phi_{\alpha\eta}}$  denotes the averaging over  $\phi_{\alpha\eta}$ , and the assumption of Eq. (6) is used. The procedure to derive Eq. (13) is analogous to that for 1D distribution function  $h_{\alpha\eta}^D(|\mathbf{k}|)$  (Refs. 45–47). If  $\psi_{\alpha'\eta'}^D(\mathbf{k})$  in Eq. (13) is defined as

$$-\beta \psi_{\alpha'\eta'}^D(\mathbf{k}) = \tilde{c}_{\alpha'\eta'}^D(k^{\rho}, k^z), \quad (14)$$

then the same formula as Eq. (1) is obtained. Note that Eq. (1) is derived without the assumption of Eq. (6), whereas Eq. (13) is derived using the assumption. Equation (14) is therefore the definition of  $\psi_{\alpha'\eta'}^D$  for the time-dependent 2D distribution function.

Using Eq. (14), the following equation is derived from Eq. (10):

$$\begin{aligned} h_{\alpha\eta}(k^{\rho}, k^z, t) &= \langle \hat{h}_{\alpha\eta}(\mathbf{k}, t) \rangle_{\Gamma, \phi_{\alpha\eta}} \\ &= \sum_{\alpha'\eta'} w_{\alpha\alpha'}(k^{\rho}, k^z) \tilde{c}_{\alpha'\eta'}^S(k^{\rho}, k^z) [\omega_{\eta'\eta}^V(|\mathbf{k}|) + n^V h_{\eta'\eta}^V(|\mathbf{k}|)] \\ &\quad + w_{\alpha\alpha'}(k^{\rho}, k^z) \{ \tilde{c}_{\alpha'\eta'}^S(k^{\rho}, k^z) - \tilde{c}_{\alpha'\eta'}^P(k^{\rho}, k^z) \} s_{\eta'\eta}^V(|\mathbf{k}|, t). \end{aligned} \quad (15)$$

Here,  $\hat{h}_{\alpha\eta}(\mathbf{k}, t)$  in Eq. (15) is defined by rewriting  $\mathbf{r}_{\alpha\eta i}$  in Eq. (9) as  $\mathbf{r}_{\alpha\eta i}(t) (= \mathbf{r}_{\eta i}(t) - \mathbf{r}_{\alpha})$ , where  $\mathbf{r}_{\eta i}(t)$  is the position

of  $\eta_i$  at time  $t$ .  $s_{\eta'\eta}^V(|\mathbf{k}|, t)$  in Eq. (15) is the van Hove function of bulk solvent

$$s_{\eta'\eta}^V(|\mathbf{k}|, t) = \frac{1}{\mathcal{V}} \int d\mathbf{\Gamma} f^V(\mathbf{\Gamma}) n^V \hat{h}_{\eta'}(\mathbf{k}, t) \hat{h}_{\eta}(-\mathbf{k}), \quad (16)$$

where  $\mathcal{V}$  is the system volume, and  $\hat{h}_{\eta}(\mathbf{k}, t)$  is defined by rewriting  $\mathbf{r}_{\alpha\eta i}$  in Eq. (9) as  $\mathbf{r}_{\eta i}(t)$ .

To calculate  $s_{\eta'\eta}^V$ , here we use the SSSV equation,<sup>42,43</sup>

$$\begin{aligned} \frac{\partial}{\partial t} s^V(|\mathbf{k}|, t) &= -|\mathbf{k}|^2 D^V \\ &\quad \times [\{\omega^V(|\mathbf{k}|)\}^{-1} - n^V \tilde{\mathbf{c}}^V(|\mathbf{k}|)] \cdot \mathbf{s}^V(|\mathbf{k}|, t), \end{aligned} \quad (17)$$

where  $\mathbf{s}^V$  has the element  $s_{\eta'\eta}^V$ ,  $D^V$  is the diffusion coefficient, and the matrix elements of  $\omega^V$  and  $\tilde{\mathbf{c}}^V$  are the intramolecular and direct correlation functions of bulk solvent, respectively. The SSSV equation can be analytically solved by using the inverse Laplace transformation for some simple cases such as a triatomic molecule.<sup>42</sup>

Utilizing the same procedure of deriving Eq. (3) from Eq. (1), Eq. (15) is rewritten to deal with the identity of the



units as follows:

$$h_{\alpha\eta}(k^\rho, k^z, t) = \sum_{\alpha'\eta'} W_{\alpha\alpha'}(k^\rho, k^z) \tilde{c}_{\alpha'\eta'}^S(k^\rho, k^z) [\omega_{\eta'\eta}^V(|\mathbf{k}|) + n^V h_{\eta'\eta}^V(|\mathbf{k}|)] + W_{\alpha\alpha'}(k^\rho, k^z) \{ \tilde{c}_{\alpha'\eta'}^S(k^\rho, k^z) - \tilde{c}_{\alpha'\eta'}^P(k^\rho, k^z) \} s_{\eta'\eta}^V(|\mathbf{k}|, t). \quad (18)$$

Equation (18) is the central equation in this study for the time-dependent 2D distribution near the interface. In the equation,  $W_{\alpha\alpha'}\{\tilde{c}_{\alpha'\eta'}^S - \tilde{c}_{\alpha'\eta'}^P\}$  describes the perturbation affecting the solvent due to the P→S transition, where the geometrical information of the wall is expressed by  $W_{\alpha\alpha'}$ .  $s^V$  describes the response of solvent to the perturbation.

The procedure of the present theory is as follows.  $h_{\eta'\eta}^V$  is calculated with the RISM equation for bulk solvent. The renormalized potentials,  $\tilde{c}_{\alpha'\eta'}^S$  and  $\tilde{c}_{\alpha'\eta'}^P$ , are calculated with the 2D-RISM theory (Eqs. (3) and (5)). The van Hoff function  $s_{\eta'\eta}^V$  at time  $t$  is calculated by the SSSV equation (Eq. (17)). Using these obtained functions ( $h_{\eta'\eta}^V$ ,  $s_{\eta'\eta}^V$ ,  $\tilde{c}_{\alpha'\eta'}^S$ ,  $\tilde{c}_{\alpha'\eta'}^P$ ), Eq. (18) is solved, and thereby  $g_{\alpha\eta}(\rho_{\alpha\eta}, z_{\alpha\eta}, t)$  ( $= h_{\alpha\eta}(\rho_{\alpha\eta}, z_{\alpha\eta}, t) + 1$ ) is obtained.

Now, we summarize the features of the present theory. Although the SSSV equation is not appropriate to treat the short-time region ( $t < 0.1$  ps), the SSSV equation analytically yields the van Hove function at arbitrary time  $t$  within the same computational cost.<sup>42,43</sup> In addition, the solution of Eq. (18) converges to the solution of Eq. (3) for the state S at  $t \rightarrow \infty$ . In other words, the present theory has the advantage in treating the long-time region. It is complementary feature with MD simulation that has an advantage in treating short-time dynamics.

### III. COMPUTATIONAL DETAIL

2D Fourier transform to solve the present equation consists of the Hankel transform with respect to  $\rho$  and 1D Fourier transform with respect to  $z$ . The Hankel transform is performed using Talman's algorithm.<sup>50</sup> The number of grid points along  $\rho$  is 512 with the spacing of  $\Delta \ln(\rho/\rho_0) = 0.02$ , where  $\rho_0$  is 1 bohr. The minimum of  $\rho$ ,  $\rho_{\min}$ , is set to  $\ln(\rho_{\min}/\rho_0) = -5.12$ . The number of grid points along  $z$  is 4096 with the spacing of  $\Delta z = 0.02$  bohr. To apply our theory to a charged wall, Ng's method<sup>51</sup> is employed. These details of the transforms are the same as the previous study.<sup>41</sup>

The system treated here consists of a single wall immersed in water solvent. Atomic sites of the wall are arranged in accord with the face of a cubic lattice. The lattice constant ( $a$ ) is 1.5 Å and the Lennard-Jones parameters of the atomic sites are  $\sigma = 1.500$  Å and  $\epsilon = 0.101$  kcal mol<sup>-1</sup>.<sup>41</sup> The number of unit  $N$  is set to 625 ( $= 25^2$ ). It was checked that the peak height of distribution is almost unchanged when  $N$  is larger than or equal to 625.<sup>41</sup> For solvent water molecule, simple point charge like model is employed (oxygen site;  $\sigma_O = 3.166$  Å and  $\epsilon_O = 0.155$  kcal mol<sup>-1</sup>, hydrogen site;  $\sigma_H = 1.000$  Å and  $\epsilon_H = 0.056$  kcal mol<sup>-1</sup>).<sup>52</sup> The diffusion coefficient of water is set to  $2.3 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>, which is the experimental data.<sup>53</sup> Calculations are carried out at 298.15 K

and the number density of water solvent of  $n^V = 0.033426$  Å<sup>-3</sup>.

In the following, we rewrite  $g_{\alpha\eta}(\rho_{\alpha\eta}, z_{\alpha\eta}, t)$  as  $g_O(\rho, z, t)$  or  $g_H(\rho, z, t)$  for simplicity, where  $g_O(\rho, z, t)$  and  $g_H(\rho, z, t)$  are time-dependent 2D-PCFs of the wall site–solvent oxygen site and the wall site–solvent hydrogen site, respectively.

## IV. RESULTS AND DISCUSSIONS

### A. Distribution of oxygen

Figure 2 shows the contour map of  $g_O(\rho, z, t)$ , where each atomic site of the wall is suddenly charged to  $-0.04213 |e|$  at  $t = 0$  s, corresponding to the surface charge density of  $-0.3$  C m<sup>-2</sup>. The distributions at  $t = 0$  s and  $t = \infty$  s are, of course, identical to those around the neutral and charged walls, respectively.<sup>41</sup> The peak at  $z = 2$  Å corresponds to the first solvation shell, and the height is 3.78 ( $\rho = 0.9$  Å and  $z = 2.0$  Å) at  $t = 0$  s. As the time proceeds, the peak becomes slightly higher to 3.86 ( $t = 1$  ps), and finally reaches to 4.01 ( $t = \infty$  s). This peak becomes monotonously higher as the time proceeding. Another maximum at  $z \sim 5$  Å corresponds to the second solvation shell. Similar to the first solvation shell, the distribution also increases as the time proceeds, and the area with  $g_O > 1.2$  is gradually expanded. These increases of the

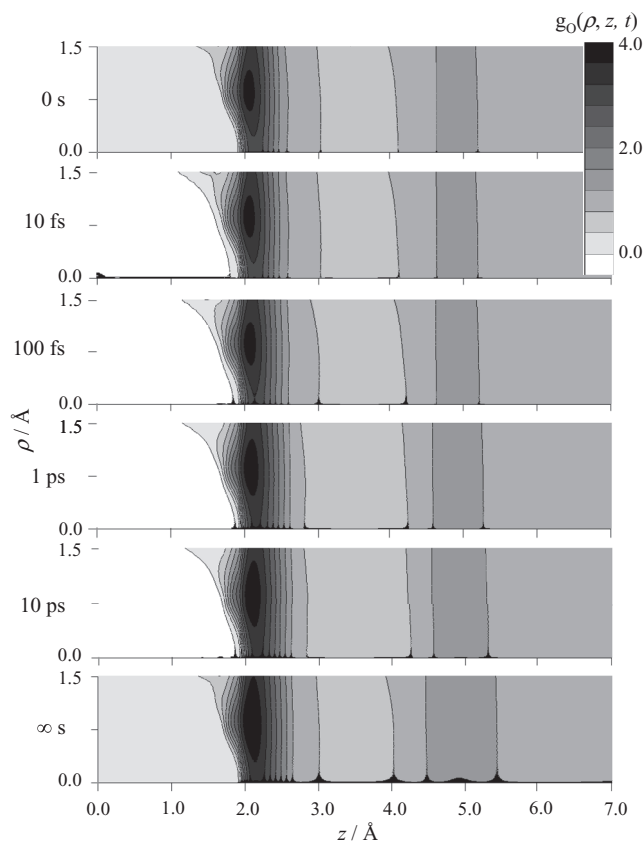


FIG. 2. Contour map of time-dependent 2D-PCFs between wall site and oxygen site. From top to bottom, the distributions are at  $t = 0$  s,  $t = 10$  fs,  $t = 100$  fs,  $t = 1$  ps,  $t = 10$  ps,  $t = \infty$  s, respectively.

distribution of solvent water in the first and second solvation shells suggest that water molecules tend to be attracted to the wall as the time proceeds. At the short range region ( $z < 2 \text{ \AA}$ ), distribution with  $g_O < 0$  (shown by white color) is found. For example,  $g_O$  at  $t = 100 \text{ fs}$  has minimum at  $z = 0 \text{ \AA}$ , and the mean value in the core region ( $z = 0 \text{ \AA}$  and  $\rho < 1.5 \text{ \AA}$ ) is  $-0.2$ . As shown in the following discussion,  $g_H$  has also the negative value, and the mean value at  $t = 100 \text{ fs}$  in the core region ( $z = 0 \text{ \AA}$  and  $\rho < 0.8 \text{ \AA}$ ) is  $-0.1$ . As noted by Raineri *et al.*, this type of artifact could be often observed in analytical solvation-dynamics theory.<sup>46</sup> Nishiyama *et al.* utilized surrogate description and also discussed the negative value.<sup>54,55</sup>

## B. Distribution of hydrogen

Change of the distribution of hydrogen site clearly shows the formation of ordered solvation structure. Figure 3 shows the distribution of solvent hydrogen,  $g_H(\rho, z, t)$ . At  $t = 0 \text{ s}$ , the peak is found in the area from  $z = 2.5 \text{ \AA}$  to  $3.0 \text{ \AA}$ , which is slightly distant from the first solvation shell of the oxygen site ( $z \sim 2 \text{ \AA}$ ).  $g_O(\rho, z, t = 0)$  and  $g_H(\rho, z, t = 0)$  therefore show that the hydrogen site tends to be located further from the wall than the bound oxygen.<sup>41</sup>

As the time proceeds, the distribution is noticeably changed. In particular, the change in the distribution at  $z \sim 1 \text{ \AA}$  is remarkable. Although the distribution remains mostly unchanged just after the charging ( $t = 10 \text{ fs}$ ), a small

peak appears around  $t = 100 \text{ fs}$  ( $\rho = 0.79 \text{ \AA}$  and  $z = 0.86 \text{ \AA}$ ) and becomes monotonously higher as the time proceeds;  $g_H = 0.41$  ( $t = 0 \text{ s}$ ),  $0.55$  ( $t = 10 \text{ fs}$ ),  $0.88$  ( $t = 100 \text{ fs}$ ),  $1.06$  ( $t = 1 \text{ ps}$ ),  $1.08$  ( $t = 10 \text{ ps}$ ), and finally  $1.12$  ( $t = \infty$ ). The change at  $z \sim 1 \text{ \AA}$  is mostly complete at  $t = 1 \text{ ps}$ , that is, 92 % of the total change is accomplished until  $t = 1 \text{ ps}$ . The change of distribution indicates that a contribution from another configuration (solvation structure) becomes greater, namely, one of the O–H bonds is directed perpendicular to the wall.<sup>41</sup>

The distribution of  $g_H(\rho, z, t)$  found in the area from  $z = 5 \text{ \AA}$  to  $6 \text{ \AA}$  corresponds to the second solvation shell. This distribution also changes as the time proceeds, although the change is small, only about 0.1. Comparing with the distribution at  $z \sim 1 \text{ \AA}$ , the change at  $z \sim 5 \text{ \AA}$  is slow. The value at the ridge ( $\rho = 0.79 \text{ \AA}$  and  $z = 5.4 \text{ \AA}$  are selected) remains almost unchanged until  $t = 100 \text{ fs}$  ( $g_H = 1.16$ ), and then slightly increases to  $1.19$  ( $t = 1 \text{ ps}$ ),  $1.21$  ( $t = 10 \text{ ps}$ ), and  $1.25$  ( $t = \infty \text{ s}$ ). In contrast to the first shell ( $z \sim 1 \text{ \AA}$ ), the response in the second solvation shell is relatively slow, and not completed even at  $t = 10 \text{ ps}$  (only 56%). This difference in solvation dynamics would be assigned to that the change of the second shell begins after the change of water orientation in the first shell. Similar dynamical behavior of solvent at some point distant from the interface has been reported in a series of works by Senapati *et al.*, in which the polarization relaxation near the interface was investigated with time-dependent density functional theory,<sup>24–26</sup> as well as with MD simulation.<sup>21</sup>

## V. CONCLUSION

In this study, we proposed a theory for time-dependent solvation structure near solid-liquid interface. The proposed theory is an extension of 2D-RISM theory, which is recently developed by us, and allows to describe the response of solvent molecule due to the sudden change of the wall state as the time-dependent 2D density distribution function. To treat the time dependency, the surrogate Hamiltonian description and the SSSV equation are utilized. This utilization enables the theory to access to long-time solvation dynamics.

The solvation dynamics of water solvent near the wall is investigated with the proposed theory. The distribution of oxygen corresponding to the first and second solvation shells increases by charging the wall. More conspicuous change is found in the distribution of hydrogen at  $z \sim 1 \text{ \AA}$ . This is assigned to the orientation of water molecule towards the wall. The distribution of hydrogen corresponding to the second shell shows small and slow change compared to the first shell. It is suggested that the solvation dynamics in the second shell follows the orientation of water molecule in the first solvation shell.

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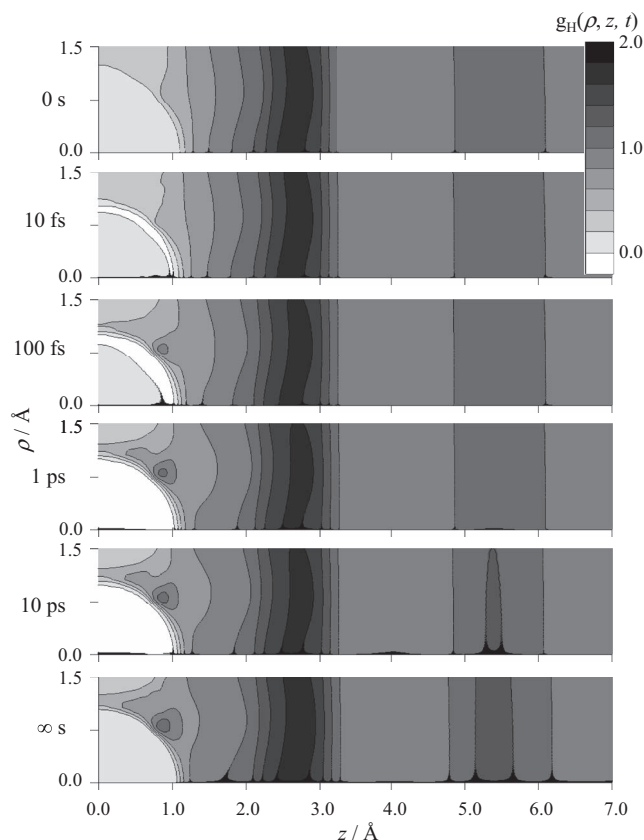


FIG. 3. Contour map of 2D-PCFs between wall site and hydrogen site. From top to bottom, the distributions are at  $t = 0 \text{ s}$ ,  $t = 10 \text{ fs}$ ,  $t = 100 \text{ fs}$ ,  $t = 1 \text{ ps}$ ,  $t = 10 \text{ ps}$ ,  $t = \infty \text{ s}$ , respectively.

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